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Transitions in Crystal Structure of Cryolite and Related Fluorides*

By E. G. Steward and H. P. Rooksby

Research Laboratories of The General Electric Company Limited, Wembley, England

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Changes in the crystal structures of cryolite and several related fluorides with temperature have been investigated by X-ray powder methods. It has been shown that cryolite, which is monoclinic at ordinary temperatures, becomes cubic at about 550° C., the lattice parameter of the structure cell being 7·95 Å. The corresponding potassium aluminium fluoride, K_3AlF_6, becomes cubic at 300° C.

The related compounds $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$, whose atomic arrangement is strictly cubic at room temperature, undergo structural deformations on cooling to $-180°$ C. The symmetry is lowered so that at low temperature these fluorides have structures similar to those of K_3AlF_6 or cryolite at room temperature. The cubic structure of elpasolite, K_2NaAlF_6, however, is maintained over the whole range of temperatures investigated. The temperature dependence of deformations from the ideal cubic atomic arrangement is briefly discussed in terms of the packing of the alkali ions in the basic three-dimensional framework of AlF_6 or FeF_6 octahedra.

The fluorides investigated are members of a single family of closely related structures to which the term 'sister-structures' used by Naray-Szabo for the perovskite family may be appropriately applied.

1. Introduction

The crystal structure of cryolite, Na_3AlF_6, has been completely determined by Naray-Szabo & Sasvari (1938). The symmetry is monoclinic and the space group $P2_1/m$. The atomic arrangement is characterized by an open framework of AlF_6 octahedra, which lie at the corners and face-centres of a nearly cubic lattice. The octahedra are, however, rotated or displaced from the highest symmetry orientation.

There are several other fluorides closely related to cryolite whose structures do conform strictly with the cubic system. Examples are ammonium iron fluoride, $(NH_4)_3FeF_6$, ammonium aluminium fluoride, $(NH_4)_3AlF_6$, and a fluoride containing both sodium and potassium, K_2NaAlF_6, of which a mineral form elpasolite is known. Further members of the family are listed in Table IXD,1 of Wyckoff's *Crystal Structures* (1951). In these cubic fluorides the octahedra, either of AlF_6 or FeF_6, are arranged as in cryolite, but no departure from high-symmetry orientation is apparent.

In some respects cryolite is noticeably pseudoisometric. Frondel (1948) has remarked upon this in the course of a study of elpasolite. He has, moreover, drawn attention to the relation between the X-ray powder diffraction patterns of elpasolite and cryolite. The stronger lines or groups of lines in the pattern of cryolite correspond roughly in position and intensity to strong lines in the pattern of the cubic elpasolite. The X-ray patterns in question are compared in Fig. 1. The similarity is a not unexpected consequence of the close underlying structural relationship between the two compounds. The greater complexity of the powder photograph of cryolite follows the departure from an ideal cubic structure, but since the departure is small, groups of lines corresponding with the single lines in the pattern of elpasolite can be distinguished, particularly in the lower-Bragg-angle region.

Some recent discussions by Donnay (1952) and Wrinch (1952) of twinning phenomena in cryolite have also emphasised its pseudo-cubic character. Indeed Wrinch remarks that 'cryolite, while not cubic, yet has a cubic character'.

The particular deformation from the cubic system characterizing the crystal structure of cryolite no doubt originates from an incompatibility in the packing of AlF_6 octahedra with sodium ions. A deformation from cubic symmetry is also manifest (Brosset, 1946) in the corresponding potassium compound, K_3AlF_6, probably for a similar reason. On the other hand, when sodium is replaced by ammonium or in part by potassium, as in elpasolite, the crystal structures become strictly cubic at ordinary temperatures. Consequently it appeared possible that through lattice expansion at temperatures above room temperature cryolite might be enabled to assume the higher symmetry condition.* Contrarily, at some temperature below room temperature the cubic structures might be forced into a lower symmetry state because of lattice contraction. The present paper gives an

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* It is mentioned by Winchell (1951) that cryolite becomes optically isotropic above 560° C.

account of investigations undertaken to explore these possibilities.

2. Nature of specimens

Both mineral and synthetic specimens of cryolite have been examined.

Two different natural cryolites were available. One sample was in powdered form, as supplied through a chemical dealer; its origin is unknown. The second sample consisted of crystal fragments from Ivigtut, Greenland, obtained from the Natural History Museum, London, through the courtesy of Dr Campbell Smith.

No natural specimen of elpasolite was available.

Synthetic preparations of Na_3AlF_6, K_3AlF_6, $(NH_4)_3AlF_6$, $(NH_4)_3FeF_6$ and K_2NaAlF_6 were made by treating the appropriate proportions of alkali and alumina with hydrofluoric acid. X-ray powder photographs were used to confirm that fluorides of the correct constitution were being prepared.

Whilst the crystalline character of the ammonium and potassium sodium compounds was such as to give good sharp X-ray powder patterns, that of the synthetic cryolite was rather less favourable and inferior to that of the natural specimens. Apart from the inferior crystalline character of the artificial cryolite specimen no differences between the X-ray powder photographs of the three specimens of cryolite could be distinguished. Lattice parameters at room temperature for the various cubic fluoride preparations are included in Table 1, and the values correspond well with those recorded in Wyckoff's *Crystal Structures* (1951).

3. Change of structures of cryolite and potassium aluminium fluoride at high temperature

The examinations at elevated temperatures were carried out in a 19 cm. diameter Unicam high-temperature powder camera.

3·1. *High-temperature study of cryolite*, Na_3AlF_6

A series of photographs were taken of powdered cryolite at successively increasing temperatures up to 550° C. The photographs disclosed not only the expected thermal expansion of the lattice, but also a progressive alteration of shape of the structure cell with increasing temperature. Relative changes in lattice parameters clearly occurred such as to make the symmetry of the structure cell approach steadily towards that of a cubic space group. Between 500 and 550° C. the departure from a cubic arrangement became rapidly smaller and at 550° C. the lines of the powder photograph fell precisely in the sequence demanded by a cubic space group. The powder photographs of cryolite at room temperature and at 550° C. are compared in Fig. 1(*B*). Above 550° C. no further change in the cubic structure cell, apart from thermal expansion, is to be expected.

The transition from a low-symmetry to a high-symmetry structure at a temperature in the neighbourhood of 550° C. was established for all the available specimens of sodium aluminium fluoride, Na_3AlF_6. Some difficulties were experienced because of a tendency to decompose under the conditions of the experiments. Perfect vacuum conditions were not obtainable in the camera, and in the course of a photographic exposure at the higher temperatures

Table 1. *Crystal structure data for cryolite and related fluorides at different temperatures*

	Data for structure cell			
	−180° C.	20° C.	300° C.	550° C.
K_2NaAlF_6	Cubic, *Pa*3 $a_0 = 8·08$ Å	Cubic, *Pa*3 $a_0 = 8·11$ Å	—	—
Na_3AlF_6 (cryolite)	—	*Monoclinic, $P2_1/m$ $a = 5·46$ Å $b = 5·61$ $c = 7·80$ $\beta = 90°\ 11'$	—	Cubic, *Fm*3*m* $a_0 = 7·95$ Å
K_3AlF_6	—	†Tetragonal $a_0 = 8·40$ Å $c_0 = 8·46$	Cubic $a_0 = 8·56$ Å	—
$(NH_4)_3AlF_6$	‡Tetragonal	Cubic, *Fm*3*m* $a_0 = 8·93$ Å	—	—
$(NH_4)_3FeF_6$	Tetragonal $a_0 = 9·03$ Å $c_0 = 9·30$	Cubic, *Fm*3*m* $a_0 = 9·10$ Å	—	—

* Data of Naray-Szabo & Sasvari (1938).
† Based on data of Brosset (1946).
‡ To a rough approximation.

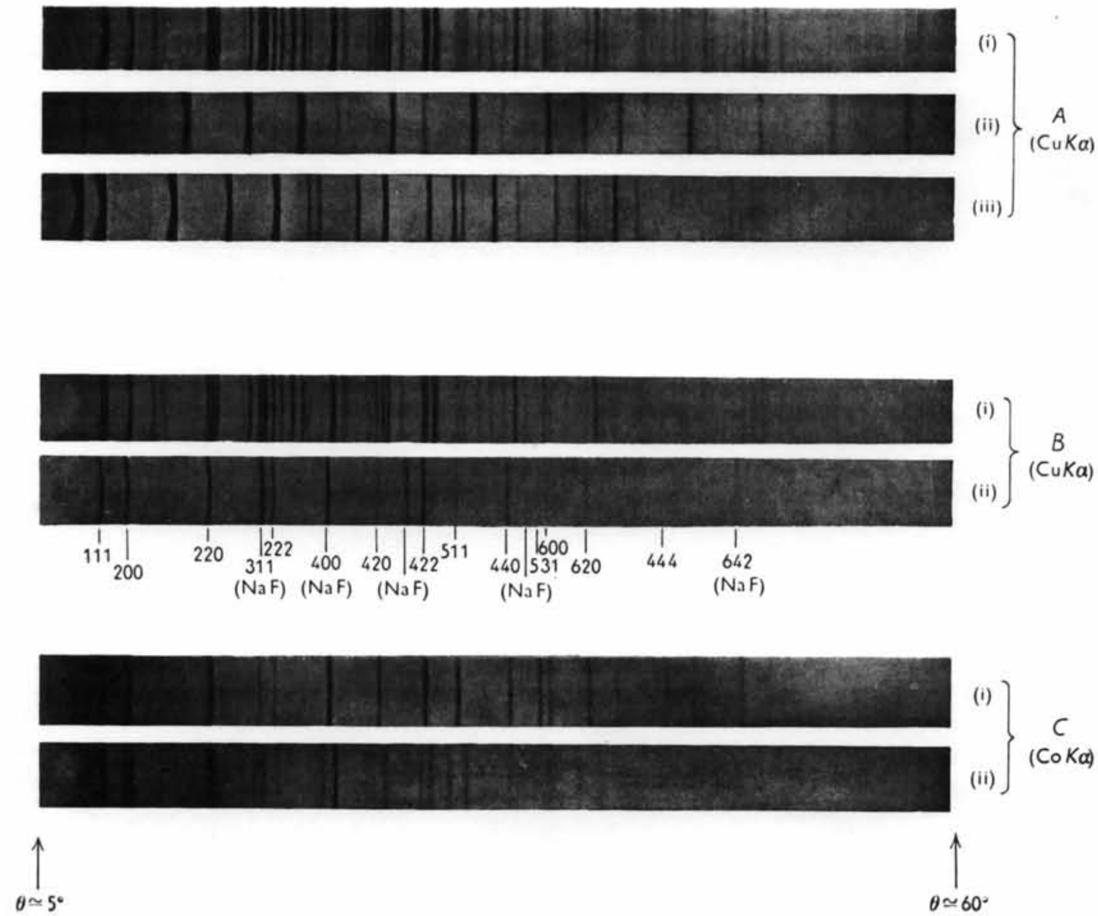

Fig. 1. X-ray powder photographs of Na_3AlF_6 & related fluorides.
A. (i) Na_3AlF_6 (cryolite), (ii) K_2NaAlF_6, (iii) $(NH_4)_3AlF_6$.
B. Na_3AlF_6 at: (i) 20° C., (ii) 550° C.
C. $(NH_4)_3FeF_6$ at: (i) 20° C., (ii) −180° C.

some formation of sodium fluoride and alumina could not be prevented. Sodium fluoride lines, for example, are indicated on the 550° C. photograph reproduced in Fig. 1(*B*(ii)).

It was confirmed that no ambiguity in the results arose from the partial decomposition. After examination of any particular specimen at a high temperature, a second photograph taken with the specimen cooled to room temperature invariably proved that that part of it remaining undecomposed gave the characteristic room-temperature X-ray pattern of cryolite. In other words, the structural transition from monoclinic to cubic symmetry was proved to be reversible.

Measurements show the cubic structure cell at 550° C. to have a lattice parameter $a_0 = 7{\cdot}95$ Å. At this temperature the structure has become strictly isomorphous with those of $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$, and the space group is $Fm3m\text{-}O_h^5$.

3·2. *High-temperature study of* K_3AlF_6

Similar experimental observations have been made on the potassium aluminium fluoride, K_3AlF_6.

The powder photograph at ordinary temperature shows line-splitting effects that demonstrate a distinct departure from an ideal cubic arrangement, but of a magnitude indicating that the departure is relatively small. Brosset (1946) postulates a body-centred tetragonal structure cell with $a_0' = 5{\cdot}94$, $c_0' = 8{\cdot}46$ Å. This may well be the simplest structure cell, but the close analogy with other members of the family is made more obvious if the atomic arrangement is described by a larger face-centred cell with $a_0 = 8{\cdot}40$, $c_0 = 8{\cdot}46$ Å, where $a_0 = \sqrt{2}.a_0'$.

At higher temperatures the tetragonal deformation is reduced, and at 300° C. line splitting on the powder photograph vanishes, so that the high-symmetry cubic structure cell is assumed. At 300° C. the lattice parameter is 8·56 Å. On cooling to room temperature the tetragonal deformation reappeared.

4. Changes of structure in $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$ at low temperatures

Following the observations on cryolite and potassium cryolite at elevated temperatures, it appeared a logical step to explore the effect of lattice contraction on the structures of those fluorides which have cubic symmetry at ordinary temperatures.

X-ray photographs were taken of the various available specimens at liquid-air temperature using the method suggested by Lonsdale & Smith (1941). A modified powder camera, as described by Tombs (1952), was used for the purpose.

For the compound K_2NaAlF_6 the powder photograph at −180° C. disclosed the normal lattice contraction to be expected on cooling, but the cubic symmetry of the structure cell remained unchanged. Good definition of the powder lines at high Bragg angles confirmed that to a high degree of precision there was no structural deformation.

With the fluorides $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$, however, the low-temperature photographs disclosed that a marked structural change takes place on cooling. The powder photographs of $(NH_4)_3FeF_6$ at room temperature and at −180° C. are compared in Fig. 1(*C*). At −180° C. the powder lines become complex and many are split into two or more components. An approximate analysis of the low-order end of the photograph indicates that all lines except 111 and 222 show multiplicity, and this can be explained by a transition from cubic to tetragonal symmetry. Thus, to a first approximation the deformation appears to be more akin to that exemplified by the structure of K_3AlF_6 below 300° C., rather than by that of cryolite, Na_3AlF_6, below 550° C.

The changes in the structure of $(NH_4)_3AlF_6$ on cooling to −180° C. appear to be similar, though complexities in the low-temperature photograph not noticeable for $(NH_4)_3FeF_6$ indicate that the true symmetry is lower than tetragonal. Crystal-structure data for both fluorides at 20° C. and −180° C. respectively are included in Table 1.

It was confirmed that the transitions were reversible by rephotographing each specimen at room temperature after any given liquid-air-temperature examination. The precise temperature at which the transition first becomes noticeable has not been determined, although from the magnitude of the observed deformation at −180° C. it appears likely that it lies between 0 and −50° C.

5. Discussion of results

Crystallographic data at different temperatures for the various members of the family of fluorides considered above are recorded in Table 1. Most of the figures given are those obtained in the present investigation, but some published data are also included.

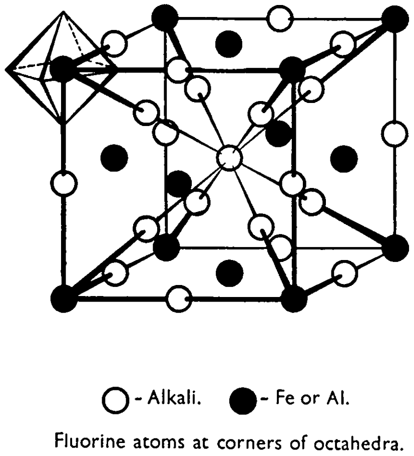

Fig. 2. Diagram representing ideal cubic atomic arrangement for fluorides of the type $(NH_4)_3FeF_6$.

The results provide a graphic illustration of the close relationships between the atomic arrangements of the various members of this family of fluorides, whatever the precise symmetry displayed at ordinary temperatures. As mentioned earlier, the basic feature of the structure is a three-dimensional framework of AlF_6 or FeF_6 octahedra with alkali ions forming links between fluorines and filling certain gaps in the network. The arrangement is depicted in the model of Fig. 2. At ordinary temperatures some members of the class maintain the ideal cubic arrangement, but in others the AlF_6 or FeF_6 octahedra become rotated or displaced out of this orientation. The present work has demonstrated that these conditions are temperature sensitive. By thermal expansion the misorientations existing at ordinary temperatures may be removed, as in the examples of cryolite and potassium aluminium fluoride. By thermal contraction the cubic arrangement characterizing the room-temperature structure may suffer distortion, as in the cases of $(NH_4)_3AlF_6$ and $(NH_4)_3FeF_6$.

The experimental proof that cryolite itself assumes a strictly cubic structure at about 550° C. is of particular interest in relation to the recent discussions by Donnay (1952) and Wrinch (1952) on cryolite twinning. It provides very positive support for the conclusion, based on morphological data, that the twin laws and operations may be completely derived by assuming pseudo-cubic symmetry.

An obvious general inference that emerges is that the temperature at which deformation from a high-symmetry structural arrangement occurs is influenced by the radius of the alkali ion. In this connection the observations on K_2NaAlF_6 are significant. For this compound, at no temperature in the range studied could any structural deformation be detected. Now in the ideal cubic atomic arrangement two kinds of sites are occupied by alkali ions. One kind is on the edges and at the centre of the large structure cell, on lines joining fluorines, whereas the other is at the centres of each of the eight small cubes of which the large structure cell is composed (Fig. 2). The numbers of these sites are in the ratio 2:1, which is exactly the ratio of potassium to sodium in K_2NaAlF_6. With two alkali ions of different radii, therefore, it may be inferred that these occupy preferred sites and in consequence a symmetrical orientation of the octahedral framework is more readily maintained than when a single alkali ion has to be packed into both kinds of atomic sites. The ordering of the sodium and potassium ions about the two kinds of sites in the structure of elpasolite was indeed established in the original structure analysis by Menzer (1932), so that the space group is actually *Pa*3 instead of *Fm*3*m*.

A similar situation to that just discussed was found to account for variations in the crystal structures of alkaline earth tungstates and molybdates of the type R_3WO_6 and R_3MoO_6 (Steward & Rooksby, 1951). The ideal space-group symmetry of the tungstates and molybdates is identical with that of the alkali aluminium and alkali iron fluorides. WO_6 or MoO_6 groups replace AlF_6 or FeF_6 groups, valencies throughout being doubled to maintain electrical neutrality.

The evidence that has been accumulated in this investigation therefore provides interesting confirmation that the alkaline earth tungstates and molybdates, of which Ca_3WO_6 may be regarded as a prototype, and the fluorides, represented by cryolite, Na_3AlF_6, form a single family of closely related structures. This family of structures contains a number which are cubic and strictly isomorphous, but in any event the relationship between these and those exhibiting some structural deformation is very close. Moreover, in many instances the structures are temperature sensitive. The term 'sister-structures', suggested by Naray-Szabo (1943) to embrace the various members of the perovskite family, appears, therefore, a particularly appropriate one to apply to the present group of compounds, including fluorides, tungstates and molybdates in the one family.

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